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(54) Title: METHOD FOR POLYMERIZING CYCLOOLEFIN POLYMER CONTAINING POLAR FUNCTIONAL GROUPS
AND ELECTRONIC DEVICES EMPLOYING THE POLYMERIZED CYCLOOLEFINS

(57) Abstract: Disclosed is a method for preparing a cycloolefin polymer containing polar functional groups, comprising: preparing a catalyst mixture including i) a precatalyst, containing a Group 10 transition metal having a ligand containing oxygen ions bonded to the metal; ii) a first cocatalyst which is an organic compound containing a Group 15 element; and iii) a second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst; and subjecting a monomer solution comprising a norbornene-based compound containing a polar functional group to an addition polymerization reaction in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-200 °C, the total amount of the organic solvent being 50-800 % by weight based on the total weight of the monomer contained in the monomer solution, and the product yield of the polymer being 50% by weight or more based on the total weight of the monomer.

METHOD FOR POLYMERIZING CYCLOOLEFIN POLYMER
CONTAINING POLAR FUNCTIONAL GROUPS AND ELECTRONIC
DEVICES EMPLOYING THE POLYMERIZED CYCLOOLEFINS

5 [Technical Field]

The present invention relates to a cycloolefin polymer, more particularly, to a method for polymerizing a high molecular weight of a cycloolefin polymer containing polar functional groups in high yield, and electronic devices employing the cycloolefin polymer.

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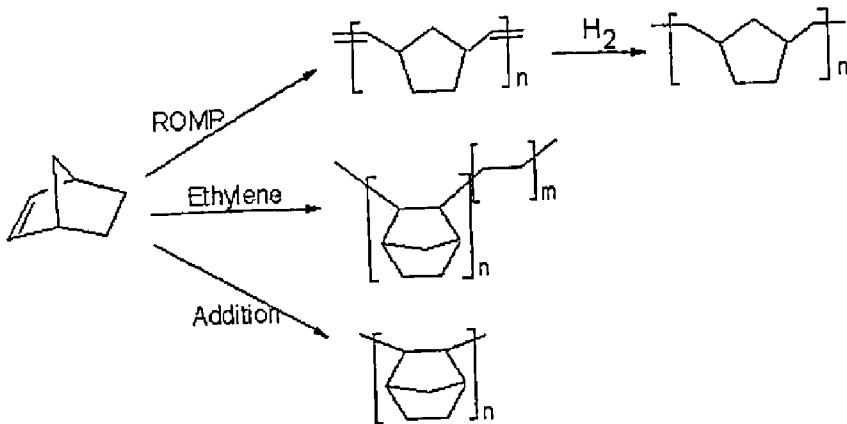
[Background Art]

Inorganic materials such as silicon oxides or nitrides have been mainly utilized in the information and electronic industries. Recent technical developments and demands for compact and high efficiency devices need new high performance materials. In this respect, a great deal of attention has been paid to polymers which have desirable physicochemical properties such as low dielectric constant and moisture absorption rate, high adhesion to metals, strength, thermal stability and transparency, and a high glass transition temperature ($T_g > 250^\circ\text{C}$).

20 Such polymers can be used as insulating films of semiconductors and TFT-LCDs, protective films of polarizing plates, multi-chip modules, integrated circuits (ICs),
25 printed circuit boards, molding materials for electronic components, optical materials, e.g., flat panel displays,

and the like. As one of new performance materials, cycloolefin polymers exhibit much improved properties than conventional olefin polymers, in that they show high transparency, heat resistance and chemical resistance, and 5 have a low birefringence and moisture absorption rate. Thus, cycloolefin polymers can be applied to various applications, e.g., optical components such as CDs, DVDs and POFs (plastic optical fibers), information and electronic components such as capacitor films and low- 10 dielectrics, and medical components such as low-absorbent syringes, blister packagings, etc.

Cycloolefin polymers are known to be prepared by one of the following three methods: ROMP (ring opening metathesis polymerization), copolymerization with ethylene, 15 and addition polymerization using catalysts containing transition metals such as Ni and Pd. These methods are depicted in Reaction Scheme 1 below. Depending on the central metal, ligand and cocatalyst of a catalyst used in the polymerization reaction, polymerization characteristics 20 and the structure and characteristics of polymers to be obtained may be varied.

Reaction Scheme 1

A Polymer prepared by the ROMP method has one double bond per one monomeric repeating unit, thus, the polymer has poor thermal and oxidative stability and is mainly used as thermosetting resins. U.S. Patent No. 5,011,730 issued to Tenny et al. discloses that such thermosetting resins are fabricated into printed circuit boards by reaction 10 injection molding.

In order to improve physicochemical properties of polymers prepared by the ROMP method, a method of hydrogenation of the ROMP-polymer in the presence of Pd or Raney-Ni catalysts has been proposed. Hydrogenated polymer 15 shows improved oxidative stability, but still needs to be improved in its thermal stability. Further, a cost increased due to additional processes is against its commercial application.

Ethylene-norbornene copolymers are known to be first synthesized using a titanium-based Ziegler-Natta catalyst 20 by Leuna, Corp., (German Patent No. 109,224 issued to

Koinzer, P. et al.). However, impurities remaining in the copolymer deteriorates its transparency and its glass transition temperature (T_g) is very low, i.e., 140 °C or lower. Although it was reported that the use of a zirconium-based metallocene catalyst enables the synthesis of high molecular weight of polymers having a narrow molecular weight distribution (Plastic News, Feb. 27, 1995, p.24), as the concentration of a cycloolefin monomer in a reaction medium increases, the catalytic activity decreases and a copolymer to be obtained has a low glass transition temperature ($T_g < 200$ °C). In addition, the copolymer has poor mechanical strength and chemical resistance, particularly against halogenated hydrocarbon solvents.

U.S. Patent No. 3,330,815 discloses a method for preparing cycloolefin polymers in the presence of a palladium-based catalyst. However, molecular weight of the cycloolefin polymer is reported to be 10,000 or less. Gaylord et al. reported a polymerization of norbornene using $[Pd(C_6H_5CN)Cl_2]_2$ as a catalyst (Gaylord, N.G.; Deshpande, A.B.; Mandal, B.M.; Martan, M. J. Macromol. Sci.-Chem. 1977, A11(5), 1053-1070). Furthermore, Kaminsky et al. reported a homopolymerization of norbornene by using a zirconium-based metallocene catalyst (Kaminsky, W.; Bark, A.; Drake, I. Stud. Surf. Catal. 1990, 56, 425). These polymers have a high crystallinity, thermally decompose at a high temperature before they melt, and are substantially insoluble in general organic solvents.

Adhesion of polymers to inorganic surfaces such as silicon, silicon oxide, silicon nitride, alumina, copper, aluminium, gold, silver, platinum, nickel, tantalum, and chromium is often a critical factor in the reliability of the polymer for use as electronic materials. US Patent No. 5 4,831,172 discloses a benzocyclobutene (BCB)-functionalized organosilane adhesive aid to increase the adhesion between an inorganic surface and a polymer.

The introduction of functional groups into a norbornene monomer enables the control of chemical and physical properties of a resultant norbornene polymer. U.S. Patent No. 3,330,815 discloses a method for producing polynorbornenes from norbornene monomers containing polar functional groups. However, catalysts are inactivated by the polar functional groups of norbornene monomers, which results in an earlier termination of the polymerization reaction, thereby producing a norbornene polymer having a molecular weight of 10,000 or less.

In an effort to overcome these problems, a method for 20 polymerizing norbornene derivatives containing polar functional groups after pretreating the norbornene derivatives with silane, alkylaluminum or borane compounds was suggested by Fink, G. et al. (Macromol. Chem. Phys. 1999, 200, 881). This method is, however, limited in the 25 introduction of the pretreated norbornenes into a polymer chain and in increasing a polymerization activity. In addition, this method further requires a post-treatment

step for removing the silane, aluminum or borane compound.

U.S. Patent No. 5,179,171 discloses a copolymer comprising polymerized units from ethylene and polymerized units from at least one cycloolefin, in which chcloolefin 5 is incorporated in the polymer chain without ring opening in the presence of a catalyst which is formed from a soluble vanadium compound and an organoaluminium compound. However, the polymer thus prepared is thermally unstable, and general physical and chemical properties of the 10 polymer, and its adhesion properties to metals are not greatly improved.

Researches have been carried out in the polymerization of norbornenes containing an ester, acetyl or silyl group, in association with the introduction of 15 polar functional groups (Risse et al., Macromolecules, 1996, Vol. 29, 2755-2763; Risse et al., Makromol. Chem. 1992, Vol. 193, 2915-2927; Sen et al., Organometallics 2001, Vol. 20, 2802-2812; Goodall et al., U.S. Patent No. 5,705,50; Lipian et al., U.S. Patent No. 6,455,650).

20 Sen et al. reported a method for polymerizing various ester norbornene monomers in the presence of a catalyst, $[Pd(CH_3CN)_4][BF_4]_2$, in which exo isomers were selectively polymerized, and the polymerization yield was low. (Sen et al., J. Am. Chem. Soc. 1981, Vol. 103, 4627-4629).

25 U.S. Patent No. 5,705,503 issued to Risse and Goodall, et al. discloses a polymer prepared from norbornenes containing polar functional groups, in which a

majority of the monomer consist of endo-isomers. However, in the polymerization reaction in which polar norbornene derivatives containing only ester groups are polymerized, the molar ratio of a catalyst to the monomers is about 5 1/100, which is economically disadvantageous.

In the polymerization reaction of polar functional norbornenes containing ester groups or acetyl groups, it has been reported that an excess of the catalyst is required (1/100 to 1/400 relative to the monomer) and the removal of the catalyst residues after polymerization is difficult. U.S. Patent No. 6,455,650 issued to Lipian et al. discloses a method for polymerizing norbornene derivatives in the presence of a small amount of a catalyst. However, the product yield in a polymerization of a polar monomer such as an ester-norbornene, is only 5%.
15

Sen et al. reported a method for polymerizing an ester-norbornene in the presence of a catalyst system including [(1,5-Cyclooctadiene)(CH₃)Pd(Cl)], PPh₃, and Na⁺[3,5-(CF₃)₂C₆H₃]₄B⁻, in which the polymerization yield of 20 ester-norbornenes is 40% or lower, the molecular weight of the polymer is 6,500 or lower, and the molar amount of the catalyst used is about 1/400 based on the monomer (Sen et al., Organometallics 2001, Vol. 20, 2802-2812).

Risse et al. reported a method for polymerizing a 25 methylester-norbornene in the presence of [(η³-allyl)PdCl]₂ and AgBF₄ or AgSbF₆ as a catalyst (Risse et al., Macromolecules, 1996, Vol. 29, 2755-2763). The

polymerization yield is about 60%, and the molecular weight of a resultant polymer is about 12,000. In addition, an excess of the catalyst of about 1/50 by mole, based on the monomer is used. The reason for the use of an excess of 5 the catalyst is explained by the fact that polar functional groups of the monomers such as ester or acetyl groups are coordinated to the active sites of the catalyst, causing steric hindrance effects preventing the norbornene derivatives from approaching onto the active sites, or 10 cationic active sites are electrically neutralized by the polar functional groups, causing a weak interaction with the double bond of norbornene (Risse et al., *Macromolecules*, 1996, Vol. 29, 2755-2763; Risse et al., *Makromol. Chem.* 1992, Vol. 193, 2915-2927).

15 Therefore, conventional methods for polymerizing cycloolefins containing polar functional groups fail to meet a certain desired level in the aspect of polymerization yield, a molecular weight of a resultant polymer, and a molar ratio of a catalyst to monomers.

20

【Disclosure of the Invention】

In one aspect, the present invention provides a method for preparing a high molecular weight of cycloolefin polymer containing polar functional groups in high yield.

25 In another aspect, the present invention provides a method for preparing a polar cycloolefin homopolymer, or copolymer comprising monomeric units of the same or

different polar functional cycloolefins, or a polar functional copolymer comprising polar and non-polar cycloolefin monomers.

In a further aspect, the present invention provides a 5 method for preparing a cycloolefin polymer containing polar functional groups which has a low dielectric constant, a low moisture absorption rate, a high glass transition temperature, a desirable thermal and oxidative stability, desirable chemical resistance, toughness and adhesion to 10 metals.

In yet another aspect, the present invention provides a method for preparing a cycloolefin polymer containing polar functional groups which has a sufficient adhesion to metal substrates such as copper, silver, gold, and the 15 like.

In still another aspect, the present invention provides a method for preparing a cycloolefin polymer containing polar functional groups which has desirable optical properties for use as optical films, protective 20 films of polarizing plates, and the like.

In still another aspect, the present invention provides a method for preparing a cycloolefin polymer containing polar functional groups which is applicable as materials for electronic components such as integrated 25 circuits (ICs), printed circuit boards and multichip modules.

In still another aspect, the present invention

provides a method for preparing a cycloolefin polymer containing polar functional groups which has a sufficient adhesion to substrates of electronic components in the absence of a coupling agent.

5 In still another aspect, the present invention provides an optical film fabricated from a cycloolefin polymer containing polar functional groups manufactured by the present method.

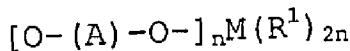
In one aspect, there is provided a method for 10 preparing a cycloolefin polymer containing polar functional groups, which comprises:

preparing a catalyst mixture including
i) a precatalyst represented by Chemical Formula 1,
containing a Group 10 transition metal having a ligand
15 containing oxygen ions bonded to the metal;
ii) a first cocatalyst which is an organic compound
containing a Group 15 element; and
iii) a second cocatalyst which is capable of
providing an anion and weakly coordinating to the metal of
20 the precatalyst; and

subjecting a monomer solution comprising a norbornene-based compound containing a polar functional group to an addition polymerization reaction in the presence of an organic solvent and the catalyst mixture, at 25 a temperature of 80-200 °C. The total amount of the organic solvent is 50-800 % by weight based on the total weight of the monomer contained in the monomer solution, and the

product yield of the polymer is 50% by weight or more based on the total weight of the monomer.

Chemical Formula 1



5 wherein

M is a Group 10 transition metal;

n is 1 or 2;

A represents a linear or branched C₁₋₂₀ alkyl, aryl, aralkyl, alkenyl group or a linear or branched C₁₋₂₀ alkyl, 10 aryl, aralkyl or alkenyl group containing a hetero atom including Si, Ge, S, O, or N;

R¹ is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl 15 group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ group containing at least one hetero atom; a C₇₋₁₅ aryl group containing at least one hetero atom; a C₆₋₄₀ aralkyl group unsubstituted or substituted with a hydrocarbon; or a C₃₋₂₀ alkynyl group.

In another aspect, the present invention provides an 20 optical anisotropic film comprising a cycloolefin polymer containing polar functional groups which has a molecular weight of 100,000 or more.

In still another aspect, there is provided a display device comprising an optical anisotropic film containing a 25 cycloolefin polymer containing polar functional groups which has a molecular weight of 100,000 or more.

Hereinafter, the present invention will now be

described in more detail.

According to the present invention, a high molecular weight of a cycloolefin polymer from a monomer mixture comprising a norbornene-based compound containing a polar functional group is prepared using a specific catalyst system in a specific condition.

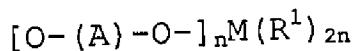
According to the present invention, a cycloolefin polymer having a molecular weight of at least 100,000 is prepared with a small amount of a catalyst in a high yield of 50% or more by weight based on the total weight of the monomers contained in the monomer mixture while maintaining the activity of the catalyst even at a high reaction temperature.

The catalyst system used in the present invention is determined to be thermally stable at a temperature of 80°C or higher in accordance with a spectroscopic analysis. While not being bound by a specific theory, it is believed that catalytic sites of the catalyst system is activated by the suppression of an interaction between polar functional groups of a cycloolefin monomer and a cationic catalyst is prevented at a high temperature, and the double bond of the cycloolefin monomer is inserted into the activated catalytic sites of the catalyst. Therefore, the polymerization reaction is not terminated until a high molecular weight of a polymer is formed.

The catalyst system of the present invention includes i) a precatalyst represented by Chemical Formula 1,

containing a Group 10 transition metal having a ligand containing oxygen ions bonded to the metal; ii) a first cocatalyst which is an organic compound containing a Group 15 element; and iii) a second cocatalyst which is capable 5 of providing an anion and weakly coordinating to the metal of the precatalyst.

Chemical Formula 1



In Chemical Formula 1,

10 M is a Group 10 transition metal;

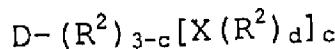
n is 1 or 2;

A represents a linear or branched C₁₋₂₀ alkyl, aryl, aralkyl, alkenyl group or a linear or branched C₁₋₂₀ alkyl, aryl, aralkyl or alkenyl group containing a hetero atom including Si, Ge, S, O, or N;

15 R¹ is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group interrupted by at least one hetero atom; a C₇₋₂₀ aryl group unsubstituted or substituted with a 20 hydrocarbon; or a C₃₋₂₀ alkynyl group.

The organic compound of the first cocatalyst has an unshared electron pair and serves as an electron donor and 25 is represented by Chemical Formula 2.

Chemical Formula 2



In Chemical Formula 2,

D is a Group 15 element,

c is an integer of 0 to 3,

X is an oxygen, sulfur, nitrogen or silicon,

d is 1 when X is an oxygen or sulfur, 2 when X is a

5 nitrogen atom, or 3 when X is a silicon,

R² is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkoxy, allyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group unsubstituted or substituted with a hydrocarbon; a C₇₋₁₅ aralkyl group unsubstituted or substituted with a hydrocarbon; a C₃₋₂₀ alkynyl group; a tri(linear or branched C₁₋₁₀ alkyl) silyl or tri(linear or branched C₁₋₁₀ alkoxy) silyl group; a tri(C₃₋₁₂ cycloalkyl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C₆₋₄₀ aryl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C₆₋₄₀ aryloxy unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C₁₋₁₀ alkyl) siloxy group; a tri(C₃₋₁₂ cycloalkyl unsubstituted or substituted with a hydrocarbon) siloxy group; or tri(C₆₋₄₀ aryl unsubstituted or substituted with a hydrocarbon) siloxy group, in which all these substituents may be substituted with a linear or branched haloalkyl group or a halogen.

Chemical Formula 3

25 (R³)₂D-(R⁴)-D(R³)₂

In Chemical Formula 3,

D is a Group 15 element,

R³ is as defined in R² of Chemical Formula 3;

R⁴ is a linear or branched C₁₋₅ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₂₀ aryl group unsubstituted or substituted with a hydrocarbon; or a C₇₋₁₅ aralkyl group 5 unsubstituted or substituted with a hydrocarbon.

The second cocatalyst is a salt represented by Chemical Formula 4.

Chemical Formula 4



10 wherein

Cation is selected from the group consisting of proton; cations of Group 1 and 2 metals; and organic groups containing these cations, to which unshared electron pairs of the organic compound of the first catalyst may be 15 bonded;

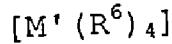
Anion is an anion capable of weakly coordinating to the metal M of the precatalyst, and is selected from the group consisting of borate, aluminate, [SbF₆], [PF₆], [AsF₆], perfluoroacetate ([CF₃CO₂]), perfluoropropionate 20 ([C₂F₅CO₂]), perfluorobutyrate ([CF₃CF₂CF₂CO₂]), perchlorate ([ClO₄]), p-toluenesulfonate ([p-CH₃C₆H₄SO₃]), [SO₃CF₃], boratabenzene, and carborane unsubstituted or substituted with a halogen atom; and

a and b are the number of the cations and anions, 25 respectively, and determined to allow the cation and anion to be electrically neutralized and balance the charges.

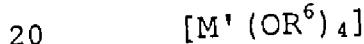
The organic group containing the cation of Chemical Formula 4 is selected from the group consisting of ammoniums $[\text{NH}(\text{R}^5)_3]^+$, $[\text{NH}_2(\text{R}^5)_2]^+$, $[\text{NH}_3(\text{R}^5)_1]^+$, and $[\text{N}(\text{R}^5)_4]^+$; phosphoniums $[\text{PH}(\text{R}^5)_3]^+$, $[\text{PH}_2(\text{R}^5)_2]^+$, $[\text{PH}_3(\text{R}^5)_1]^+$, and $[\text{P}(\text{R}^5)_4]^+$; carboniums $[\text{C}(\text{R}^5)_3]^+$; $[\text{H}(\text{OEt}_2)_2]^+$; $[\text{Ag}]^+$; and $[\text{Cp}_2\text{Fe}]^+$, in which R^5 is a linear or branched C_{1-20} alkyl group; an alkyl or silylalkyl group substituted with a halogen; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a cycloalkyl or silyl cycloalkyl group substituted with a halogen; a C_{6-40} aryl group unsubstituted or substituted with a hydrocarbon; an aryl or silyl aryl group substituted with a halogen; a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon; or an aralkyl or silyl aralkyl group substituted with a halogen.

15 . The borate or aluminate of Chemical Formula 4 is an anion represented by Chemical 4a or 4b.

Chemical Formula 4a



Chemical Formula 4b



In Chemical Formula 4a and 4b,

M' is a boron or aluminum;

R^6 is a halogen; a linear or branched C_{1-20} alkyl or alkenyl group unsubstituted or substituted with a halogen atom; a C_{3-12} cycloalkyl group unsubstituted or substituted with a halogen; a C_{6-40} aryl group which unsubstituted or substituted with a hydrocarbon; a C_{6-40} aryl group

substituted with a linear or branched C₃₋₂₀ trialkylsiloxy group or a linear or branched C₁₈₋₄₈ triarylsiloxy group; or a C₇₋₁₅ aralkyl group unsubstituted or substituted with a halogen.

5 The catalyst mixture includes a metal catalyst complex containing a cation complex made of the precatalyst and the first catalyst, and an anion complex made of the second cocatalyst.

In one embodiment of the invention, the catalyst mixture comprises, based on 1 mole of the precatalyst containing Group 10 transition metal, 1-3 moles of the first cocatalyst containing the organic compound containing the Group 15 element; and 1-2 moles of the second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst.

15 In accordance with the present invention, a catalyst mixture including a precatalyst containing a Group 10 transition metal having a ligand containing oxygen ions bonded to the metal of Chemical Formula 1, a first cocatalyst of an organic compound containing a Group 15 element and a second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst. Then, in the presence of an organic solvent and the catalyst mixture, a monomer solution comprising a norbornene-based compound containing a polar functional group is subjected to an addition polymerization reaction at a temperature of 80-200°C. The temperature for

a polymerization reaction is preferably 80-170°C and more preferably 80-150°C

Preferably, the organic solvent is selected from the group consisting of dichloromethane, dichloroethane, 5 toluene, chlorobenzene and mixtures thereof. The total amount of the organic solvent in the reaction system is 50-800 % by weight based on the total weight of the monomer contained in the monomer solution. The total amount of the organic solvent in the reaction system can be varied within 10 the defined range, for example, 50-400 % by weight, or 50-200 % by weight, based on the total weight of the monomer contained in the monomer solution.

In the polymerization reaction system, the molar ratio of the catalyst mixture based on the Group 10 15 transition metal compound to the monomers contained in the monomer solution is in the range of 1:2,500 - 1:100,000. This ratio of the catalyst to the monomers is far smaller than that used in conventional polymerization reaction system for preparing a polar cycloolefin polymer, however 20 it is sufficient to exhibit catalytic activity in the method of the present invention for preparing a high molecular weight of a cycloolefin polymer. Preferably, the molar ratio of the catalyst system to the monomers is in the range of 1: 5,000~1: 20,000, based on the Group 10 25 transition metal compound of the precatalyst.

In the present method, the catalyst is added into the polymerization reaction system in a preformed catalyst

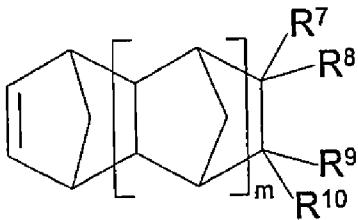
system in the form of a mixture or a complex of the respective catalyst components, i.e. the Group 10 transition metal compound, the organic compound containing a Group 15 element and the salt for providing an anion. 5 Further, each catalyst components can be directly added into the polymerization reaction system without being preformed.

In the present method, a norbornene-based compound is used for preparing a polar functional cycloolefin polymer. 10 The norbornene-based monomer or a derivative thereof refers to a monomer containing at least one norbornene (bicyclo[2.2.1]hept-2-ene)) unit represented by Chemical Formula 5 below.

The polar functional group of the nonbonene-based 15 compound contained in the monomer solution is preferably an ester group or an acetyl group.

The norbornene-based monomer containing polar functional groups may be a mixture of endo- and exo-isomers, and the composition ratio between the isomers is 20 not specifically limited.

In one embodiment of the invention, the norbornene-based compound containing a polar functional group is represented by the following Chemical Formula 5.

Chemical Formula 5

In Chemical Formula 5,

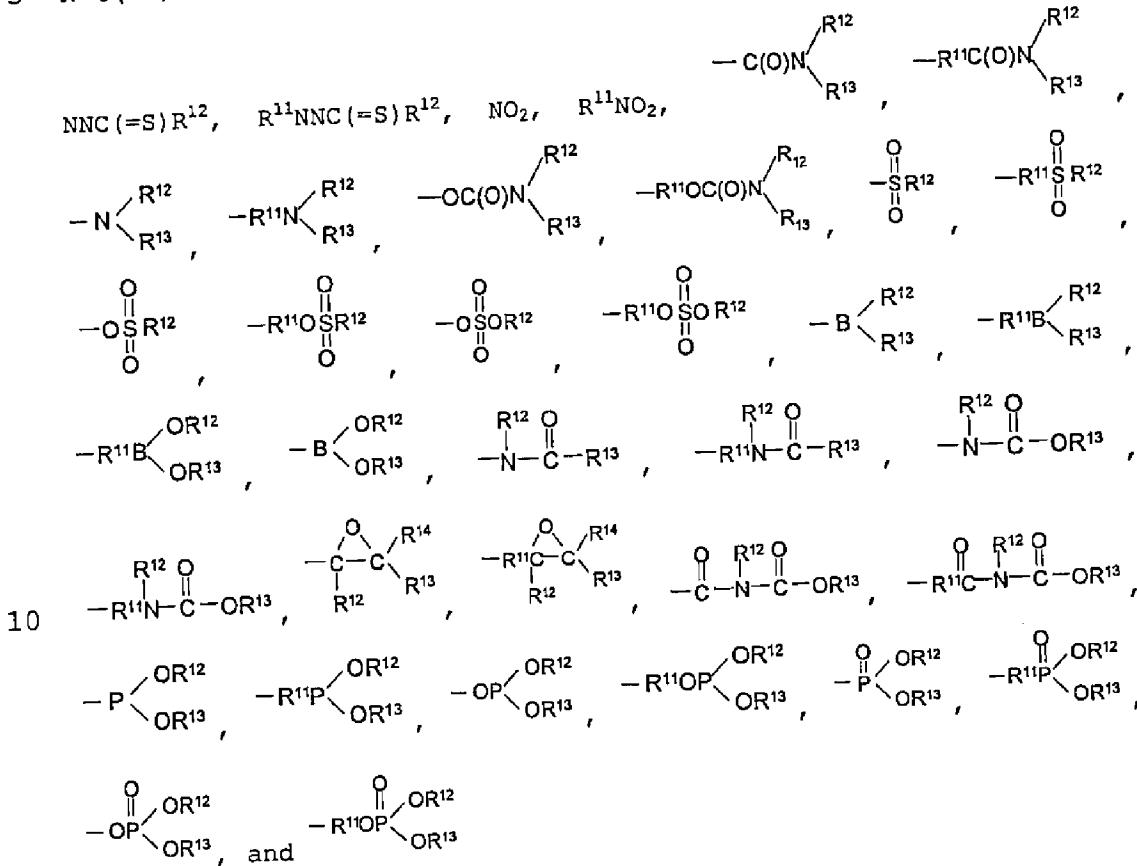
m is an integer of 0 to 4,

5 at least one of R⁷, R⁸, R⁹ and R¹⁰ is a polar functional group, the others are non-polar functional group, and R⁷, R⁸, R⁹ and R¹⁰ can be bonded together to form a saturated or unsaturated C₁₋₂₀ cyclic group or C₆₋₂₄ aromatic ring;

10 the non-polar functional group includes hydrogen; halogen; a linear or branched C₁₋₂₀ alkyl group; , a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ hoalalkenyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or 15 branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C₇₋₁₅ aralkyl group unsubstituted or substituted with 20 alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

the polar functional group is a non-hydrocarbonaceous polar group containing at least one of O, N, P, S, Si and

B, and is selected from the group consisting of: OR¹², OC(O)OR¹², R¹¹OC(O)OR¹², C(O)R¹², R¹¹C(O)R¹², OC(O)R¹², R¹¹OC(O)R¹², (R¹¹O)pOR¹², (OR¹¹)pOR¹², C(O)OC(O)R¹², R¹¹C(O)OC(O)R¹², SR¹², R¹¹SR¹², SSR¹², R¹¹SSR¹², S(=O)R¹², R¹¹S(=O)R¹², R¹¹C(=S)R¹², 5 R¹¹C(=S)SR¹², R¹¹SO₃R¹², SO₃R¹², R¹¹N=C=S, NCO, R¹¹NCO, CN, R¹¹CN,



, in which R¹¹ is a linear or branched C₁₋₂₀ alkyl group; a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl,

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alkenyl, alkynyl, halogen, haloalkyl, ~~haloalkenyl~~, or haloalkynyl; and a C₇₋₁₅ aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

5 R¹², R¹³, and R¹⁴ are each independently hydrogen; a linear halogen; a linear or branched C₁₋₂₀ alkyl group; a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ hoalalkenyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group
10 unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₇₋₁₅ aralkyl group unsubstituted or substituted with alkyl,
15 alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; or alkoxy, haloalkoxy, carbonyloxy, halocarbonyloxy; and

p is an integer of 1 to 10.

20 The monomer solution further comprises a cycloolefin compound containing no polar functional group. The molar ratio of the cycloolefin compound containing no polar functional group is 30 % by mole based on the total monomers in the monomer solution.

25 In accordance with the method of the invention, a homopolymer is prepared by polymerizing a same norbornene-based monomer containing a polar functional group, or a

copolymer including di-, tri- and multi-copolymers is prepared by polymerizing different polar functional norbornene-based monomers, or a copolymer including di-, tri- and multi-copolymers is prepared by polymerizing a 5 polar functional norbornene-based monomer and a cycloolefin monomer having no polar functional group.

In accordance with the method of the present invention, the cycloolefin polymer containing polar functional groups having a molecular weight of 100,000 or 10 more can be prepared in a yield of 50% or higher. In order to fabricate an optical film using the cycloolefin polymer, the molecular weight of the cycloolefin polymer is preferably controlled to 100,000-1,000,000.

In conventional polymerization system, cycloolefin polymers containing polar functional groups is prepared in 15 a very low yield and in a low molecular weight, whereas the present method produces a high molecular weight of a cycloolefin polymer containing polar functional groups in a high yield.

20 Further, according to the method of the present invention, the deterioration of the catalytic activity by endo-isomers containing polar functional groups can be avoided. In addition, a high yield of the cycloolefin polymer can be achieved with a small amount of the 25 catalyst. Furthermore, the norbornene-based polymer containing polar functional groups prepared in accordance with the method of the present invention is transparent,

has sufficient adhesion to metals or polymers containing different polar functional groups, thermal stability and strength, and exhibits a low dielectric constant sufficient to be used as insulating electronic materials. The cycloolefin polymer produced by the present invention has a desirable adhesion to substrates of electronic components without requiring a coupling agent, and at the same time, a sufficient adhesion to metal substrates, e.g., copper, silver and gold. Further, the cycloolefin polymer of the present invention exhibits a desirable optical properties so that it can be used as materials for protective films of polarizing plates and electronic components such integrated circuits (ICs), printed circuit boards, multichip modules, and the like.

A cycloolefin polymer containing polar functional groups prepared by the present method is fabricated into an optical anisotropic film by using a general process which is known in the art. The optical anisotropic film thus prepared has 70 to 1000 nm of a retardation value (R_{th}), as defined by the following Equation 1.

(Equation 1)

$$R_{th} = \Delta(n_y - n_z) \times d$$

In the Equation 1, n_y is a refractive index in a fast axis direction in a plane, measured at a wavelength of 550nm; n_z is a refractive index in a thickness direction,

measured at a wavelength of 550nm; and

d is the film thickness.

The refractive index of the optical anisotropic film

satisfies the following Equation 2.

5 (Equation 2)

$$n_x \approx n_y > n_z$$

In the Equation 2, n_x is a refractive index in a slow

axis direction in a plane, n_y is a refractive index in a

fast axis direction in the plane, and n_z is a refractive

10 index in a thickness direction.

The optical anisotropic film can be used as a

negative C-plate type optical compensation film for Liquid

Crystal Displays.

[Best Mode for Carrying Out the Invention]

15 Hereinafter, the present invention will be described
in more detail with reference to the following Examples.
However, these Examples are given for the purpose of
illustration and are not to be construed as limiting the
scope of the invention.

20 In the following Examples, all operations for
treating compounds sensitive to air or water were carried
out in accordance with a standard Schlenk technique or dry
box technique. Nuclear magnetic resonance spectra were

obtained using Bruker 400 and 600 spectrometers. The molecular weights and molecular weight distributions of polymers were determined by GPC (gel permeation chromatography) using standard polystyrene samples.

5 Thermal analyses, for example, TGA and DSC were performed using a TA Instrument (TGA 2050; heating rate 10 K/min).

Toluene was distilled and purified in sodium/benzophenone, and dichloromethane and chlorobenzene were distilled and purified in CaH₂.

10

Preparative Example 1: Preparation of 5-norbornene-2-carboxylic acid methylester

DCPD (dicyclopentadiene, Aldrich, 256.5 mL, 1.9 mol), methylacrylate (Aldrich, 405 mL, 4.5 mol) and hydroquinone 15 (3.2 g, 0.03 mol) were charged into a 2 L high-pressure autoclave, and the temperature was raised to 220 °C. The resulting mixture was reacted for 5 hours with stirring at 300 rpm. After the reaction was completed, the reaction mixture was cooled and transferred to a distilling apparatus. The reaction mixture was distilled under a reduced pressure (1 torr) using a vacuum pump to yield the title compound at 50 °C (yield: 57.6 %, exo/endo = 58/42).

20

¹H-NMR (600MHz, CDCl₃), endo: δ 6.17 (dd, 1H), 5.91 (dd, 1H), 3.60 (s, 3H), 3.17 (b, 1H), 2.91 (m, 1H), 2.88 (b, 1H), 1.90 (m, 1H), 1.42 (m, 2H), 1.28 (m, 1H); exo: δ 25 6.09 (m, 2H), 3.67 (s, 3H), 3.01 (b, 1H), 2.88 (b, 1H), 2.20 (m, 1H), 1.88 (m, 1H), 1.51 (d, 1H), 1.34 (m, 2H).

Preparative Example 2: Preparation of endo-rich 5-norbornene-2-carboxylic acid methylester

DCPD (dicyclopentadiene, Aldrich, 256.5 mL, 1.9 mol),
5 methylacrylate (Aldrich, 405 mL, 4.5 mol) and hydroquinone
(3.2 g, 0.03 mol) were charged into a 2 L high-pressure
autoclave, and the temperature was raised to 180 °C. The
resulting mixture was reacted for 5 hours with stirring at
300 rpm. After the reaction was completed, the reaction
10 mixture was cooled and transferred to a distilling
apparatus. The reaction mixture was distilled under a
reduced pressure (1 torr) using a vacuum pump to yield the
title compound at 50 °C (yield: 85 %, exo/endo = 41/59).

¹H-NMR (600MHz, CDCl₃), endo: δ 6.17 (dd, 1H), 5.91
15 (dd, 1H), 3.60 (s, 3H), 3.17 (b, 1H), 2.91 (m, 1H), 2.88
(b, 1H), 1.90 (m, 1H), 1.42 (m, 2H), 1.28 (m, 1H); exo: δ
6.09 (m, 2H), 3.67 (s, 3H), 3.01 (b, 1H), 2.88 (b, 1H),
2.20 (m, 1H), 1.88 (m, 1H), 1.51 (d, 1H), 1.34 (m, 2H).

20 Preparative Example 3: Preparation of 5-norbornene-2-

carboxylic acid butylester

DCPD (dicyclopentadiene, Aldrich, 180 mL, 1.34 mol),
butylacrylate (Junsei, 500 mL, 3.49 mol) and hydroquinone
(2.7 g, 0.025 mol) were charged into a 2 L high-pressure
25 autoclave, and the temperature was raised to 190 °C. The
resulting mixture was reacted for 5 hours with stirring at
300 rpm. After the reaction was completed, the reaction

mixture was cooled and transferred to a distilling apparatus. The reaction mixture was distilled under a reduced pressure (1 torr) using a vacuum pump to yield the title compound at 80 °C (yield: 78 %, exo/endo = 55/45).

5 ¹H-NMR (600MHz in CDCl₃): 6.12(m,2H), 4.09(t,2H),
3.17(s,1H), 3.04(s,1H), 2.92(m,1H), 2.20(m,1H), 1.90(m,1H),
1.60(m,2H), 1.40(m,4H), 0.94(t,3H)

Preparative Example 4: Preparation of 5-norbornene-2-

10 carboxylic acid benzyl ester

DCPD (dicyclopentadiene, Aldrich, 67.32 mL, 0.5 mol), benzyl acrylate (Lancaster, 163 g, 1.0 mol) and hydroquinone (0.23 g, 2.1 mmol) were charged into a 2 L high-pressure autoclave, and the temperature was raised to 15 200 °C. The resulting mixture was reacted for 5 hours with stirring at 300 rpm. After the reaction was completed, the reaction mixture was cooled and transferred to a distilling apparatus. The reaction mixture was distilled twice under a reduced pressure (1 torr) using a vacuum pump to yield 20 the title compound at 190 °C (yield: 65 %, exo/endo = 56/44).

25 ¹H-NMR (600 MHz, CDCl₃): δ 7.32 (m, 5H), 6.15~6.07 (m, 2H), 5.11~5.04 (m, 2H), 3.02~2.88 (m, 2H), 2.96 & 2.20 (m, 1H), 1.92 (m, 2H), 1.52~1.22 (m, 1H), 1.38 (m, 1H)

25

Preparative Example 5: Preparation of 5-norbornene-2-

allylacetate

DCPD (dicyclopentadiene, Aldrich, 248 mL, 1.852 mol), allylacetate (Aldrich, 500 mL, 4.63 mol) and hydroquinone (0.7 g, 0.006 mol) were charged into a 2 L high-pressure autoclave, and the temperature was raised to 190 °C. The resulting mixture was reacted for 5 hours with stirring at 300 rpm. After the reaction was completed, the reaction mixture was cooled and transferred to a distilling apparatus. The reaction mixture was distilled twice under a reduced pressure (1 torr) using a vacuum pump to yield the title compound at 56 °C (yield: 30 %, exo/endo = 57/43).

¹H-NMR (600 MHz, CDCl₃): δ 6.17~5.91 (m, 2H), 4.15~3.63 (m, 2H), 2.91~2.88 (m, 2H), 2.38 (m, 1H), 2.05 (s, 3H), 1.83 (m, 1H), 1.60~1.25 (m, 2H), 0.57 (m, 1H).

15 Preparative Example 6: Synthesis of (allyl)Pd(acac)

(Allyl)Pd(acac) was synthesized according to Imamura et al. (Bull. Chem. Soc. Jpn., 1969, Vol. 42, 805) and Jackson et al. (Aust. J. Chem., 1978, Vol. 31, 1073). [(allyl)PdCl]₂ (1.83 g, 5.0 mmol) and sodium acetylacetone (1.22 g, 10 mmol) were charged into a 250 mL Schlenk flask, and benzene (50ml) was added thereto. The resulting mixture was reacted for about 1 hour at a room temperature. After the reaction was completed, the solvent was removed and a pure (allyl)Pd(acac) were obtained (yield 85 %, 1.04 g).

Example 1: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane (catalyst: Pd(acac)₂, the molar ratio of the catalyst to borate cocatalyst was 1:2)

5 Pd(acetylacetonate)₂ (acetylacetonate = acac, 3.5 mg, 11 µmol), dimethyl aniliniumtetrakis(pentafluorophenyl) borate (17.6 mg, 22 µmol) and tricyclohexylphosphine (3.0 mg, 11 µmol) as catalysts were charged into a 250 mL Schlenk flask in a dry box, and then 5 ml of dichloromethane was added thereto. 5-norbornene-2-
10 carboxylic acid methylester (MENB, 10 mL, 55.6 mmol) prepared in Preparative Example 1 was added to the flask at room temperature. While the reaction temperature was raised to 90 °C the dichloromethane was removed under partial vacuum. Thereafter, the reaction mixture was reacted at 90 °C for 18 hours. The reaction mixture became viscous with the passage of time, and finally hardened after 10 hours. After the reaction was completed, 50 ml of toluene was added into the viscous solution to dilute it.
15 The solution was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in vacuo at 80 °C for 24 hours to yield 7.06 g of the polymer of 5-norbornene-2-carboxylic acid methylester (67.5 % by weight, based on the total weight of the monomer).
20
25

Examples 2 to 4: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane at various polymerization temperatures (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

Polymers of 5-norbornene-2-carboxylic acid methylester were prepared in the same manner as described in Example 1, except that the molar ratios of the amount of Pd(acac)₂ as a catalyst to the monomer were changed to 5,000:1 and 10,000:1, as shown in Table 1, and the polymerization temperatures were changed to 100 and 110°C. The results are shown in Table 1 below.

Table 1

Example Nos.	Monomer (mL)	Monomer/Pd (mol)	Temperature (°C)	Time (h)	Yield		Mw	Mw/Mn
					[g]	[%]		
Example 1	MENB(10)	5000/1	90	18	7.06	67.5	185,100	2.16
Example 2	MENB(10)	5000/1	100	10	7.98	76.3	166,300	2.15
Example 3	MENB(10)	5000/1	110	10	8.30	79.4	149,400	2.45
Example 4	MENB(17)	10000/1	110	10	13.57	76.3	155,800	2.13

Example 5: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

Pd(acac)₂ (4mg), dimethyl aniliniumtetrakis (pentafluorophenyl) borate (21.1 mg) and tricyclohexylphosphine (3.7 mg) as catalysts were charged into a 250 mL Schlenk flask in a dry box, and then 5 ml of 5 dichloromethane was added thereto. 5-norbornene-2-carboxylic acid methylester (10 mL) prepared in Preparative Example 1 was added to the flask at room temperature. The reaction temperature was raised to 80 °C and the reaction mixture was reacted at 80 °C for 18 hours. After the 10 reaction was completed, 50 ml of toluene was added into a hardened polymer to dissolve it. The solution was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in vacuo at 80 °C for 24 hours to yield 15 6.75 g of the polymer of 5-norbornene-2-carboxylic acid methylester (66.8 % by weight, based on the total weight of the monomer). The molecular weight (Mw) of the polymer was 100,400, and Mw/Mn was 1.93

20 Example 6: Polymerization of 5-norbornene-2-
carboxylic acid methylester in dichloromethane (catalyst:
Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst
was 1:1)

25 7.43 g (71.0 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester was prepared in the same manner as described in Example 1, except that 8.8 mg (11 µmol) of

dimethyl aniliniumtetrakis (pentafluorophenyl) borate was used. The molecular weight of the polymer (Mw) was 184,500, and Mw/Mn was 2.08.

5 Example 7: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:1)

10 7.95 g (76.0 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester was prepared in the same manner as described in Example 6, except that the polymerization temperature was changed to 100 °C. The molecular weight of the polymer (Mw) was 181,800 and Mw/Mn was 2.13.

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Example 8: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane (catalyst: Pd(acetate)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

20 8.95 g (85.6 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester was prepared in the same manner as described in Example 1, except that Pd(acetate)₂ (2.5 mg, 11 µmol) was used in place of Pd(acac)₂. The molecular weight 25 of the polymer (Mw) was 195,300 and Mw/Mn was 2.3.

Example 9: Polymerization of 5-norbornene-2-carboxylic acid methylester in dichloromethane (catalyst: (allyl)Pd(acac), molar ratio of the catalyst to borate cocatalyst was 1:2)

5 8.5 g (81.3 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester was prepared in the same manner as described in Example 1, except that (allyl)Pd(acac) (2.7 mg, 11 µmol) was used in place of Pd(acac)₂. The molecular
10 weight of the polymer (Mw) was 185,000 and Mw/Mn was 2.2.

Example 10: Polymerization of endo-rich 5-norbornene-2-carboxylic acid methylester in dichloromethane at 90 °C (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

15 Pd(acac)₂ (3.4 mg, 11 µmol), dimethyl aniliniumtetrakis (pentafluorophenyl) borate (17.6 mg, 22 µmol) and tricyclohexylphosphine (3.0 mg, 11 µmol) as catalysts were charged into a 250 mL Schlenk flask in a dry
20 box, and then 3ml of dichloromethane was added thereto. Endo-rich 5-norbornene-2-carboxylic acid methylester (10 mL, 55.6 mmol) prepared in Preparative Example 2 was added to the flask at room temperature. After the reaction
25 temperature was raised to 90 °C the reaction mixture was reacted at 90 °C for 18 hours. After the reaction was completed, 50 ml of toluene was added into the viscous solution to dilute it. The solution was poured into an

excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 80 °C for 24 hours to yield 7.03 g of the polymer of 5-norbornene-2-carboxylic acid methylester (67.2 5 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 167,898, and M_w/M_n was 2.3.

Example 11: Polymerization of endo-rich 5-norbornene-
10 2-carboxylic acid methylester in dichloromethane at 100 °C
(catalyst: $Pd(acac)_2$, molar ratio of the catalyst to borate
cocatalyst was 1:2)

6.9 g (66.0 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester was prepared in the same manner as described in Example 10, except that the polymerization temperature was changed to 100 °C. The molecular weight of the polymer (M_w) was 157,033 and M_w/M_n was 2.4.

20 Examples 12 to 14: Polymerization of 5-norbornene-2-carboxylic acid butylester in dichloromethane at various polymerization temperatures (catalyst: $Pd(acac)_2$, molar ratio of the catalyst to borate cocatalyst was 1:2)

Polymers of 5-norbornene-2-carboxylic acid butylester were prepared in the same manner as described in Example 1, except that 5-norbornene-2-carboxylic acid butylester were used as the monomer, and the polymerization temperatures

were changed to 90, 100 and 120 °C as shown in Table 2. The results are shown in Table 2 below.

Table 2

5

Example Nos.	Monomer (mL)	Temperature (°C)	Time (h)	Yield		Mw	Mw/Mn
Example 12	BENB(20)	90	18	14.02	72.1	186,200	2.07
Example 13	BENB(20)	100	10	18.43	95.0	157,100	1.88
Example 14	BENB(20)	120	4	16.30	84.0	130,000	1.85

Examples 15 to 17: Polymerization of 5-norbornene-2-carboxylic acid butylester in chlorobenzene at various polymerization temperatures (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

10 Polymers of 5-norbornene-2-carboxylic acid butylester were prepared in the same manner as described in Example 12, except that chlorobenzene was used as a solvent in place of dichloromethane, and the polymerization 15 temperatures were changed to 90, 100 and 110 °C as shown in Table 3. The results are shown in Table 3 below.

Table 3

Example Nos.	Monomer (mL)	Temperature (°C)	Time (h)	Yield		Mw	Mw/Mn
Example 15	BENB(20)	90	18	12.86	66.1	149,400	2.02
Example 16	BENB(20)	100	18	14.37	73.9	138,700	2.00
Example 17	BENB(20)	110	18	17.28	88.9	13,800	1.96

Examples 18 and 19: Polymerization of 5-norbornene-2-carboxylic acid butylester in toluene at various polymerization temperatures (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

Polymers of 5-norbornene-2-carboxylic acid butylester were prepared in the same manner as described in Example 12, except that toluene was used as a solvent in place of dichloromethane, and the polymerization temperatures were changed to 90 and 100 °C as shown in Table 4. The results are shown in Table 4 below.

15 Table 4

Example Nos.	Monomer (mL)	Monomer/Toluene	Temperature (°C)	Time (h)	Yield		Mw	Mw/Mn
Example 18	BENB(20)	2/1	90	18	11.66	60.0	128,100	1.94
Example 19	BENB(20)	2/1	100	18	15.69	80.7	120,300	1.93

Example 20: Polymerization of 5-norbornene-2-

carboxylic acid butylester in dichloromethane at 90°C
(catalyst: Pd(acetate)₂, molar ratio of the catalyst to
borate cocatalyst was 1:2)

Pd(acetate)₂ (4.5 mg, 20 µmol), dimethyl anilinium
5 tetrakis(pentafluorophenyl) borate (32.0 mg, 40 µmol) and
tricyclohexylphosphine (5.6 mg, 20 µmol) as catalysts were
charged into a 250 mL Schlenk flask in a dry box, and then
5 ml of dichloromethane was added thereto. 5-norbornene-2-
carboxylic acid butylester (20 mL, 100 mmol) prepared in
10 Preparative Example 3 was added to the flask at room
temperature. While the reaction temperature was raised to
90 °C the dichloromethane was removed under partial vacuum.
The reaction mixture was reacted at 90 °C for 18 hours. The
reaction mixture became viscous with the passage of time,
15 and finally hardened after 10 hours. After the reaction
was completed, 50 ml of toluene was added into the viscous
solution to dilute it. The solution was poured into an
excess of ethanol to precipitate a white polymer, which was
filtered through a glass funnel, washed with ethanol, and
20 dried in vacuo at 80 °C for 24 hours to yield 10.02 g of the
polymer of 5-norbornene-2-carboxylic acid butylester (51.5
% by weight, based on the total weight of the monomer).
The molecular weight of the polymer (Mw) was 153,033, and
Mw/Mn was 2.4.

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Example 21: Polymerization of 5-norbornene-2-
carboxylic acid butylester in dichloromethane at 100°C

(catalyst: Pd(acetate)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

18.4 g (92.8 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid butylester was prepared in the same manner as described in Example 20, except that the polymerization temperature was changed to 100 °C. The molecular weight of the polymer (Mw) was 148,200 and Mw/Mn was 2.2.

10 Example 22: Polymerization of 5-norbornene-2-carboxylic acid butyl in dichloromethane (catalyst: (allyl)Pd(acac), molar ratio of the catalyst to borate cocatalyst was 1:2)

12.06 g (62.0 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid butylester was prepared in the same manner as described in Example 20, except that (allyl)Pd(acac) (2.7 mg, 11 µmol) was used in place of Pd(acetate)₂. The molecular weight of the polymer (Mw) was 142,000 and Mw/Mn was 2.5.

25 Example 23: Copolymerization of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic acid butylester in dichloromethane (catalyst: Pd(acac)₂, mass production)

Pd(acac)₂ (1.39 g), dimethyl aniliniumtetrakis(pentafluorophenyl) borate (1.28 g) and tricyclohexyl

phosphine (1.28 g) as catalysts were charged into a 500 mL Schlenk flask in a dry box, and then 300 ml of dichloromethane was added thereto. 5-norbornene-2-carboxylic acid methylester (1046 g) prepared in 5 Preparative Example 1, 5-norbornene-2-carboxylic acid butylester (3082 g) prepared in Preparative Example 3, and toluene (8300 g) were charged into a mass reactor at room temperature and the temperature of the mixture was raised to 80 °C. At this temperature, the catalyst mixture was 10 added to the mass reactor and the polymerization reaction was continued for 90 hours during which the viscosity of the reaction mixture was increased. After the polymerization reaction was completed, 10 kg of toluene was 15 added into the viscous solution to dilute it. The solution was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 80 °C for 24 hours to yield 2.2 kg of the copolymer of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic acid 20 butylester (53.8 % by weight, based on the total weight of the monomer). The molecular weight (Mw) of the copolymer was 115,000, and Mw/Mn was 1.6.

Example 24: Copolymerization of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic acid butylester in dichloromethane (catalyst: Pd(acac)₂, 25 molar ratio of the catalyst to borate cocatalyst was 1:2)

Pd(acac)₂ (6.0 mg, 20 µmol), dimethyl aniliniumtetrakis (pentafluorophenyl) borate (32.0 mg, 40 µmol) and tricyclohexyl phosphine (5.6 mg, 20 µmol) as catalysts were charged into a 250 mL Schlenk flask in a dry box, and then 5ml of dichloromethane was added thereto. 5-norbornene-2-carboxylic acid methylester (9 ml, 50 mmol) prepared in Preparative Example 1, 5-norbornene-2-carboxylic acid butylester (10 ml, 50 mmol) prepared in Preparative Example 3 were added to the flask at room temperature and the temperature of the mixture was raised to 100°C during which the dichloromethane was removed under partial vacuum. While the polymerization was carried at that temperature for 18 hours, the viscosity of the reaction mixture was increased. After the polymerization reaction was completed, 50 ml of toluene was added into the viscous solution to dilute it. The solution was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in vacuo at 80 °C for 24 hours to yield 16.02 g of the copolymer of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic acid butylester (83.7 % by weight, based on the total weight of the monomer). The molecular weight (Mw) of the copolymer was 182,300 and Mw/Mn was 2.13.

25

Example 25: Copolymerization of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic

acid butylester in dichloromethane at 110 °C (catalyst: Pd(acac)₂, molar ratio of the catalyst to borate cocatalyst was 1:2)

17.8 g (92.8 % by weight, based on the total weight
5 of the monomer) of the polymer of 5-norbornene-2-carboxylic acid methylester and 5-norbornene-2-carboxylic acid butylester was prepared in the same manner as described in Example 24, except that the polymerization temperature was changed to 110 °C. The molecular weight of the polymer (Mw)
10 was 164,600 and Mw/Mn was 2.43.

Example 26: Polymerization of 5-norbornene-2-allylacetate in toluene (catalyst: Pd(acac)₂)

5-norbornene-2-allylacetate (5.0 g, 30.1 mmol)
15 prepared in Preparative Example 5 and toluene (10 ml) were charged into a 250 ml Schlenk flask. A catalyst solution (dichloromethane: 3 ml) including Pd(acac)₂ (1.83 mg, 6.0 µmol), tricyclohexylphosphine (1.69 mg, 6.0 µmol), and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (9.64 mg, 12.0 µmol) was added to the flask. The reaction mixture was reacted with stirring at 90 °C for 18 hours. After the polymerization reaction was completed, 50 ml of toluene was added into the viscous solution to dilute it. The solution was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in vacuo at 80 °C for 24 hours to yield 4.79 g of a polymer of 5-

norbornene-2-allylacetate (95.8 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 203,000 and M_w/M_n was 2.6.

5 Example 27: Polymerization of 5-norbornene-2-allylacetate in toluene (catalyst: Pd(acetate)₂)

5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (10 ml) were added into a 250 ml Schlenk flask. A catalyst solution (dichloromethane: 1 ml) including Pd(acetate)₂ (1.4 mg, 6.2 μ mol), tricyclohexylphosphine (1.9 mg, 6.8 μ mol), and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (10.0 mg, 13.6 μ mol) was added to the flask. The reaction mixture was reacted with stirring at 90 °C for 4 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 4.45 g of the polymer of 5-norbornene-2-allylacetate (86.7 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 279,618 and M_w/M_n was 3.23.

25 Example 28: Polymerization of 5-norbornene-2-allylacetate in toluene (catalyst: Pd(acetate)₂)

5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (15 ml) were

added into a 250 ml Schlenk flask. A catalyst solution (dichloromethane: 1 ml) including Pd(acetate)₂ (0.7 mg, 3.1 μ mol), tricyclohexylphosphine (1.0 mg, 3.4 μ mol), and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (5.4 mg, 6.8 μ mol) was added to the flask. The reaction mixture was reacted with stirring at 90 °C for 6 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed 10 with ethanol, and dried in vacuo at 65 °C for 24 hours to yield 4.70 g of the polymer of 5-norbornene-2-allylacetate (91.6 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (Mw) was 484,033 and Mw/Mn was 3.11.

15

Example 29: Polymerization of 5-norbornene-2-allylacetate in toluene (catalyst: Pd(acetate)₂)

5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (15 ml) were 20 added into a 250 ml Schlenk flask. A catalyst solution (dichloromethane: 1 ml) including Pd(acetate)₂ (0.46 mg, 2.1 μ mol), tricyclohexylphosphine (0.64 mg, 2.3 μ mol), and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (3.6 mg, 4.5 μ mol) was added to the flask. The reaction mixture 25 was reacted with stirring at 80 °C for 8 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white

polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 4.44 g of the polymer of 5-norbornene-2-allylacetate (86.5 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (Mw) was 472,666 and Mw/Mn was 3.03.

Example 30: Polymerization of 5-norbornene-2-allylacetate in a high pressure reactor (catalyst:
10 Pd(acetate)₂)

5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (15 ml) were charged into a high pressure reactor with a stirrer. A catalyst solution (dichloromethane: 1 ml) including 15 Pd(acetate)₂ (0.7 mg, 3.1 µmol), tricyclohexylphosphine (1.0 mg, 3.4 µmol), and dimethyl aniliniumtetrakis (pentafluorophenyl) borate (5.4 mg, 6.8 µmol) was added to the reactor. The reaction mixture was reacted with stirring at 130 °C for 6 hours. After the polymerization 20 reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 4.51 g of the polymer of 5-norbornene-2-allylacetate (87.9 % by weight, based on the total weight of the monomer). The 25 molecular weight of the polymer (Mw) was 368,200 and Mw/Mn was 3.11.

Example 31: Polymerization of 5-norbornene-2-allylacetate in a high pressure reactor (catalyst: Pd(acetate)₂)

5 5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (15 ml) were charged into a high pressure reactor with a stirrer. A catalyst solution (dichloromethane: 1 ml) including Pd(acetate)₂ (0.7 mg, 3.1 µmol), tricyclohexylphosphine 10 (1.0 mg, 3.4 µmol), and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (5.4 mg, 6.8 µmol) was added to the reactor. The reaction mixture was reacted with stirring at 150 °C for 6 hours. After the polymerization reaction was completed, the reaction mixture was poured 15 into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in *vacuo* at 65 °C for 24 hours to yield 4.17 g of the polymer of 5-norbornene-2-allylacetate (81.2 % by weight, based on the total weight of the monomer). The 20 molecular weight of the polymer (M_w) was 273,500 and M_w/M_n was 3.42.

Example 32: Polymerization of 5-norbornene-2-allylacetate in a high pressure reactor (catalyst: Pd(acetate)₂)

25 5-norbornene-2-allylacetate (5.0 ml, 30.9 mmol) prepared in Preparative Example 5 and toluene (15 ml) were

charged into a high pressure reactor with a stirrer. A catalyst solution (dichloromethane: 1 ml) including Pd(acetate)₂ (0.7 mg, 3.1 µmol), tricyclohexylphosphine (1.0 mg, 3.4 µmol), and dimethyl aniliniumtetrakis 5 (pentafluorophenyl) borate (5.4 mg, 6.8 µmol) was added to the reactor. The reaction mixture was reacted with stirring at 170 °C for 6 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, 10 which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 3.82 g of the polymer of 5-norbornene-2-allylacetate (74.4 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 175,400 and M_w/M_n 15 was 3.52.

Example 33: Polymerization of 5-norbornene-2-allylacetate in dichloromethane at 90 °C (catalyst: (allyl)Pd(acac))

20 5.6 g (56.0 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-allylacetate was prepared in the same manner as described in Example 28, except that (allyl)Pd(acac) was used as the catalyst in place of Pd(acetate)₂. The molecular weight of the polymer 25 (M_w) was 141,000 and M_w/M_n was 2.3.

Example 34: Copolymerization of 5-norbornene-2-

carboxylic acid methylester and 5-norbornene-2-allylacetate
in toluene (catalyst: Pd(acetate)₂, 5-norbornene-2-
carboxylic acid methylester / 5-norbornene-2-allylacetate =
1/2)

5 5-norbornene-2-carboxylic acid methylester (5.89 g, 38.7 mmol) prepared in Preparative Example 1, 5-norbornene-2-allylacetate (15.0 g, 90.2 mmol) prepared in Preparative Example 5 and toluene (41 mL) were added into a 250 mL Schlenk flask. A catalyst solution (dichloromethane: 5 ml) 10 including Pd(acetate)₂ (2.89 mg, 13.0 µmol), tricyclohexylphosphine (3.62 mg, 13.0 µmol) and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (20.66 mg, 26.0 µmol) was added to the flask. The reaction mixture was reacted with stirring at 90 °C for 18 hours. After the 15 polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 10.48g of the copolymer of 5-norbornene-2-carboxylic 20 acid methylester and 5-norbornene-2-allylacetate (50.2 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (Mw) was 144,000 and Mw/Mn was 2.4.

25 Example 35: Copolymerization of 5-norbornene-2-
carboxylic acid methylester and norbornene (catalyst:
Pd(acac)₂)

5-norbornene-2-carboxylic acid methylester (16.74 g) prepared in Preparative Example 1, norbornene (4.44 g) and toluene (37 mL) were added into a 250mL Schlenk flask. Pd(acetate)₂ (4.79 mg) and tricyclohexylphosphine (4.41 mg) 5 in toluene (5 mL) and dimethyl aniliniumtetrakis (pentafluorophenyl) borate (25.2 mg) in dichloromethane (2 mL) were added to the flask. The reaction mixture was reacted with stirring at 90 °C for 18 hours. After the polymerization reaction was completed, the reaction mixture 10 was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried in vacuo at 65 °C for 24 hours to yield 12.96 g of the copolymer of 5-norbornene-2-carboxylic acid methylester and norbornene (61.2 % by weight, based on 15 the total weight of the monomer). The molecular weight of the polymer (Mw) was 164,000 and Mw/Mn was 2.02.

Example 36: Copolymerization of 5-norbornene-2-carboxylic acid methylester and butylnorbornene (catalyst:
20 Pd(acac)₂)

5-norbornene-2-carboxylic acid methylester (14.64 g) prepared in Preparative Example 1, butylnorbornene (6.14 g) and toluene (37 mL) were added into a 250mL Schlenk flask. Pd(acac)₂ (4.19 mg) and tricyclohexylphosphine (4.41 mg) in 25 toluene (5 mL), and dimethyl aniliniumtetrakis (pentafluorophenyl) borate (25.2 mg) in dichloromethane (2 mL) were added to the flask. The reaction mixture was

reacted with stirring at 90 °C for 18 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed 5 with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 12.08 g of the copolymer of 5-norbornene-2-carboxylic acid methylester and butylnorbornene (58.1 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 116,000 and M_w/M_n was 1.97.

10

Example 37: Copolymerization of 5-norbornene-2-acetate and hexylnorbornene (catalyst: Pd(acac)₂)

5-norbornene-2-acetate (13.57 g), hexylnorbornene (6.82 g) and toluene (42 mL) were added into a 250mL 15 Schlenk flask. Pd(acac)₂ (3.9 mg) and tricyclohexylphosphine (3.6 mg) in toluene (5 mL) and dimethyl aniliniumtetrakis (pentafluorophenyl) borate (20.4 mg) in dichloromethane (2 ml) were added to the flask. The reaction mixture was reacted with stirring at 90 °C for 18 20 hours. After the polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 10.4 g of the copolymer of 5- 25 norbornene-2-acetate and hexylnorbornene (51.0 % by weight, based on the total weight of the monomer). The molecular weight of the polymer (M_w) was 231,000 and M_w/M_n was 2.11.

Example 38: Copolymerization of 5-norbornene-2-allylacetate and butylnorbornene (catalyst: Pd(acac)₂)

5-norbornene-2-allylacetate (8.2 g) prepared in
5 Preparative Example 1, butylnorbornene (3.2 g) and toluene
(47 mL) were added into a 250mL Schlenk flask. A catalyst
solution (toluene: 5 mL) including Pd(acac)₂ (3.2 mg),
tricyclohexylphosphine (4.0 mg) and dimethylanilinium
tetrakis (pentafluorophenyl) borate (40.0 mg) were added to
10 the flask. The reaction mixture was reacted with stirring
at 90 °C for 18 hours. After the polymerization reaction
was completed, the reaction mixture was poured into an
excess of ethanol to precipitate a white polymer, which was
filtered through a glass funnel, washed with ethanol, and
15 dried in vacuo at 65 °C for 24 hours to yield 8.85 g of the
copolymer of 5-norbornene-2-carboxylic acid methylester and
butylnorbornene (77.8 % by weight, based on the total
weight of the monomer). The molecular weight of the
polymer (Mw) was 198,300 and Mw/Mn was 3.44.

20

Example 39: Copolymerization of 5-norbornene-2-carboxylic acid butylester and phenylnorbornene (catalyst: Pd(acetate)₂)

5-norbornene-2-carboxylic acid butylester (9.19 g)
25 prepared in Preparative Example 3, phenylnorbornene (4.5 g)
and toluene (30 mL) were added into a 250 mL Schlenk flask.
A catalyst solution (dichloromethane: 3 mL) including

Pd(acac)₂ (1.98 mg), tricyclohexylphosphine (2.47 mg) and dimethyl aniliniumtetrakis(pentafluorophenyl) borate (14.1 mg) were added to the flask. The reaction mixture was reacted with stirring at 90 °C for 18 hours. After the 5 polymerization reaction was completed, the reaction mixture was poured into an excess of ethanol to precipitate a white polymer, which was filtered through a glass funnel, washed with ethanol, and dried *in vacuo* at 65 °C for 24 hours to yield 8.28 g of the copolymer of 5-norbornene-2-carboxylic acid methylester and butylnorbornene (60.5 % by weight, based on the total weight of the monomer). The molecular 10 weight of the polymer (Mw) was 132,000 and Mw/Mn was 2.69.

Comparative Example 1: Polymerization of 5-norbornene-2-carboxylic acid butylester in dichloromethane
15 (catalyst: Pd(acac)₂)

1.23 (6.4 % by weight, based on the total weight of the monomer) of the polymer of 5-norbornene-2-carboxylic acid butylester was prepared in the same manner as 20 described in Example 11, except that the polymerization temperature was changed to 60 °C

Comparative Examples 2 to 4: Polymerization of 5-norbornene-2-carboxylic acid butylester at various
25 polymerization temperatures in dichloromethane (catalyst: Pd(acac)₂)

Polymers of 5-norbornene-2-carboxylic acid butylester

were prepared in the same manner as described in Example 11, except that the polymerization temperatures were changed to 65, 70, and 75, respectively, as shown in Table 5 below. The results are shown in Table 5.

5 Table 5

Comparative Example Nos.	Monomer (mL)	Temperature (°C)	Time (h)	Yield		Mw	Mw/Mn
				[g]	[%]		
Comparative Example 1	BENB(20)	60	18	1.23	6.4	124,600	1.54
Comparative Example 2	BENB(20)	65	18	1.30	6.7	134,200	1.67
Comparative Example 3	BENB(20)	70	18	1.52	7.8	137,100	1.68
Comparative Example 4	BENB(20)	75	18	2.15	11.1	146,100	1.88

Comparative Example 5: Polymerization of 5-norbornene-2-carboxylic acid methylester (catalyst: [(allyl)PdCl]₂, molar ratio of monomers to catalyst was 10 4000:1)

[(allyl)PdCl]₂ (6.0 mg), lithiumtetrakis (pentafluorophenyl) borate (22.5 mg) and tricyclohexylphosphine (12.0 mg) as catalysts were charged into a 100mL Schlenk flask in a dry box, and then 5ml of toluene was added thereto. 5-norbornene-2-carboxylic acid methylester (10mL) and toluene (20 ml) were added into a 250 ml Schlenk flask. At room temperature the catalyst mixture was added into the monomer solution, and then the reaction temperature was raised to 90 °C and the reaction mixture was reacted at 90 °C for 18 hours. Then, the

reaction mixture was poured into an excess of ethanol. A polymer precipitate was not detected.

Comparative Example 6: Polymerization of 5-norbornene-2-carboxylic acid butylester (molar ratio of monomers to catalyst was 500:1)

[$(\text{allyl PdCl})_2$] (18.8 mg), lithiumtetrakis (pentafluorophenyl) borate (70.6 mg) and tricyclohexylphosphine (36.1 mg) as catalysts were charged into a 100mL Schlenk flask in a dry box, and then 5ml of toluene was added thereto. 5-norbornene-2-carboxylic acid butylester (5 mL) and toluene (20 ml) were added into a 250 ml Schlenk flask. At room temperature the catalyst mixture was added into the monomer solution, and then the reaction temperature was raised to 90 °C and the reaction mixture was reacted at 90 °C for 18 hours. Then, the reaction mixture was poured into an excess of ethanol. A polymer precipitate was not detected.

Comparative Example 7: Polymerization of 5-norbornene-2-carboxylic acid butylester (molar ratio of monomers to catalyst was 100:1)

[$(\text{allyl PdCl})_2$] (188 mg), lithiumtetrakis (pentafluorophenyl) borate (1.06 g) and tricyclohexylphosphine (361 mg) as catalysts were charged into a 100mL Schlenk flask in a dry box, and then 10 ml of toluene was added thereto. 5-norbornene-2-carboxylic acid

butylester (10 mL) and toluene (20 ml) were added into a 250 ml Schlenk flask. At room temperature the catalyst mixture was added into the monomer solution, and then the reaction temperature was raised to 90 °C and the reaction 5 mixture was reacted at 90 °C for 18 hours. Then, the reaction mixture was poured into an excess of ethanol. A polymer precipitate was not detected.

As can be seen from Comparative Examples 1-4, 10 polymerization reaction below 80 °C polymers having molecular weights of 100,000 or more were obtained, however the polymerization yields were very low. In Comparative Examples 5-7, polymer was not obtained from polymerization of ester norbornenes in the presence of catalysts having a 15 hydrocarbyl-based ligand coordinated thereto. It is believed that such catalysts used in Comparative Examples 5-7 are not so thermally stable as those used in Examples having oxygen-containing ligands, so that they are inactivated by functional groups of the monomers at a high 20 temperature. Therefore, according to the present invention, the catalyst having an oxygen-containing ligand is stable at a high temperature of 80°C or higher, and is not inactivated by functional groups of cycloolefin monomers, allowing the production of cycloolefin polymer 25 having a high molecular weight of 100,000 or higher.

Examples 40 - 42: Preparation of film using a cycloolefin

polymer containing polar functional groups

Each of the polymers prepared in Examples 4, 19, and 25 was mixed with a solvent to form a coating solution as shown in Table 6. The coating solution was cast on a glass 5 substrate using a knife coater or a bar coater. Then, the substrate was dried at room temperature for 1 hour, and further dried at 100 °C for 18 hours. The glass plate was kept at -10 °C for 10 seconds, and the film on the glass plate was peeled with a knife to obtain a transparent film 10 whose thickness variation was below 2%. The optical transmittance and thicknesses of the films at 400 to 800nm are shown in Table 6.

Optical anisotropy

The refractive index (n) of each transparent film was 15 measured with an Abbe refractometer. The phase difference inside the film (R_e) was measured with an automatic birefringence meter (Wang Ja Instruments; KOBRA-21 ADH). The phase difference of the film thickness direction and the x-axis direction inside the film (R_{th}) was calculated by 20 the following Equation 2, after measuring the phase difference when the angle between the incident light and

the film plane was 50° (R_θ).

[Equation 2]

$$R_{th} = \frac{R_\theta \times \cos \theta_f}{\sin^2 \theta_f}$$

The difference of refractive indices ($n_x - n_y$) and ($n_y - n_z$) were calculated by dividing R_e and R_{th} values by the film thickness. ($n_x - n_y$), R_θ , R_{th} , and ($n_y - n_z$) values of each transparent film are shown in Table 6.

Table 6

Classification	Composition of film solution		Physical properties of film					
	Polymer (parts by weight)	Solvent (parts by weight)	Thickness (μm)	Optical transmittance (%)	n (refractive index)	($n_x - n_y$) $\times 10^3$	R_{th} (nm/μm)	($n_y - n_z$) $\times 10^3$
Example 40	Polymer (Ex. 4) 100	THF, 560	114	92	1.52	0.008	5.78	5.78
Example 41	Polymer (Ex. 19) 100	MC:360 TL: 200	120	92	1.50	0.009	2.13	2.13
Example 42	Polymer (Ex. 25) 100	TL: 560	103	91	1.51	0.012	3.29	3.29

In Table 6, THF stands for tetrahydrofuran, MC stands for methylene chloride, and TL stands for toluene.

When the triacetate cellulose film ($n_y > n_z$) was

overlapped to measure the R_θ value, all R_θ values of each film increased. This indicates that the films have negative birefringence ($n_y > n_z$) in the film thickness direction.

5 The refractive index of the optical anisotropic film satisfies the following equation 3.

(Equation 3)

$$n_x \approx n_y > n_z$$

In the Equation 3, n_x is a refractive index in a slow 10 axis direction in a plane, n_y is a refractive index in a fast axis direction in the plane, and n_z is a refractive index in a thickness direction.

Refractive index in the thickness direction of an anisotropic optical film made of the polymer of the present 15 invention can be varied according to the control of the types and content of functional groups introduced in the polymer. Thus, the anisotropic film can be used as optical compensation films for various display devices including liquid crystal display.

Example 43: Adhesion property of butyl ester norbornene homopolymer film to PVA polarizing film

A polymer film was prepared from the polymer of 5-norbornene-2-carboxylic acid butylester prepared in Example 19. The polymer film was corona-treated 3 times at a line speed of 6 m/min with 80 mA, and then the contact angle was measured. For water, the contact angle was 20.7°, and for diiodomethane, it was 22°. The surface tension was calculated as 76.9 m·N/m.

Within 30 minutes after the corona treatment, a sufficiently-dried PVA polarizing film (iodine type, transmittivity: 44%) was roll-pressed with 10wt% of PVA solution. Then, it was dried at 80 °C for 10 minutes. The 15 PVA polarizing panel with the butyl ester norbornene polymer film roll-pressed thereon showed a very good adhesion property.

According to the present invention, a high yield can be obtained by controlling the reaction temperature and 20 reaction time of Diels-Alder reaction of exo-rich norbornene-ester based monomer comprising more than 50 mol%

of exo norbornene-ester monomers. When the exo-rich norbornene-ester monomer is polymerized in the presence of a Group X transition metal catalyst system with a specific ligand, a norbornene-ester based addition polymer having a large molecular weight can be obtained in high yield. The prepared norbornene-ester based addition polymer has superior optical characteristics so as to be used for a protection film of a polarizer, a retardation film, or a glass substrate, and has good adhesivity to a variety of substrates.

【Industrial Applicability】

According to the method of the present invention, the deterioration of the catalytic activity by endo-isomers containing polar functional groups can be avoided. In addition, cycloolefin polymers can be produced in a high yield with the use of a small amount of the catalyst. Furthermore, since the cycloolefin polymer containing polar functional groups prepared in accordance with the method of the present invention is transparent and has sufficient adhesion to metals or polymers containing different polar functional groups and enhanced thermal stability and strength, it can be used as an insulating electronic material. Further, an isotropic optical film made of the polar functional cycloolefin polymer produced by the

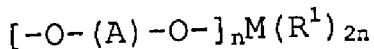
present method can be used as compensation films for various display devices because its refractive index in a thickness direction can be controlled depending on the types and contents of functional groups introduced in the 5 polymer.

While the present invention has been described with reference to the particular illustrative embodiment, it is not to be restricted by the embodiment but only by the appended claims. It is to be appreciated that those 10 skilled in the art can change or modify the embodiments without departing from the scope and spirit of the present invention.

What is claimed is:

1. A method for preparing a cycloolefin polymer containing polar functional groups, comprising:
 - 5 preparing a catalyst mixture including
 - i) a precatalyst represented by Chemical Formula 1, containing a Group 10 transition metal having a ligand containing oxygen ions bonded to the metal;
 - ii) a first cocatalyst which is an organic compound containing a Group 15 element; and
 - 10 iii) a second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst; and
 - subjecting a monomer solution comprising a
 - 15 norbornene-based compound containing a polar functional group to an addition polymerization reaction in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-200 °C the total amount of the organic solvent being 50-800 % by weight based on the total weight
 - 20 of the monomer contained in the monomer solution, and the product yield of the polymer being 50% by weight or more based on the total weight of the monomer.

Chemical Formula 1



25

wherein

M is a Group 10 transition metal;

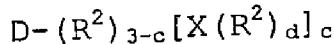
n is 1 or 2;

A represents a linear or branched C₁₋₂₀ alkyl, aryl, aralkyl, alkenyl group or a linear or branched C₁₋₂₀ alkyl, aryl, aralkyl or alkenyl group containing a hetero atom including Si, Ge, S, O, or N;

R¹ is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group containing at least one hetero atom; a C₇₋₁₅ aralkyl group unsubstituted or substituted with a hydrocarbon; or a C₃₋₂₀ alkynyl group.

2. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the organic compound of the first cocatalyst has an unshared electron pair and serves as an electron donor and is represented by Chemical Formula 2:

20 Chemical Formula 2



wherein

D is a Group 15 element,

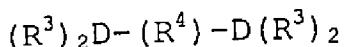
25 c is an integer of 0 to 3,

X is an oxygen, sulfur, nitrogen or silicon,

d is 1 when X is an oxygen or sulfur, 2 when X is a nitrogen atom, or 3 when X is a silicon,

R² is hydrogen; a linear or branched C₁₋₂₀ alkyl, alkoxy, allyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₄₀ aryl group unsubstituted or substituted with a hydrocarbon; a C₇₋₁₅ aralkyl group unsubstituted or substituted with a hydrocarbon; a tri(linear or branched C₁₋₁₀ alkyl) silyl or tri(linear or branched C₁₋₁₀ alkoxy) silyl group; a tri(C₃₋₁₂ cycloalkyl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C₆₋₄₀ aryl unsubstituted or substituted with a hydrocarbon) silyl group; a tri(C₆₋₄₀ aryloxy unsubstituted or substituted with a hydrocarbon) silyl group; a tri(linear or branched C₁₋₁₀ alkyl) siloxy group; a tri(C₃₋₁₂ cycloalkyl unsubstituted or substituted with a hydrocarbon) siloxy group; or tri(C₆₋₄₀ aryl unsubstituted or substituted with a hydrocarbon) siloxy group, in which all these substituents may be substituted with a linear or branched haloalkyl group or a halogen.

20 Chemical Formula 3



wherein

D is a Group 15 element,

R³ is as defined in R² of Chemical Formula 3;

25 R⁴ is a linear or branched C₁₋₅ alkyl, alkenyl or vinyl group; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with a hydrocarbon; a C₆₋₂₀ aryl group unsubstituted or substituted with a hydrocarbon; or a C₇₋₁₅ aralkyl group

unsubstituted or substituted with a hydrocarbon.

3. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1,
5 wherein the second cocatalyst is a salt represented by Chemical Formula 4:

Chemical Formula 4



10 wherein

Cation is selected from the group consisting of proton; cations of Group 1 and 2 metals; and organic groups containing these cations, to which unshared electron pairs of the organic compound of the first catalyst may be
15 bonded;

Anion is an anion capable of weakly coordinating to the metal M of the precatalyst, and is selected from the group consisting of borate, aluminate, $[\text{SbF}_6]$, $[\text{PF}_6]$, $[\text{AsF}_6]$, perfluoroacetate ($[\text{CF}_3\text{CO}_2]$), perfluoropropionate ($[\text{C}_2\text{F}_5\text{CO}_2]$), perfluorobutyrate ($[\text{CF}_3\text{CF}_2\text{CF}_2\text{CO}_2]$), perchlorate ($[\text{ClO}_4]$), p-toluenesulfonate ($[\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3]$), $[\text{SO}_3\text{CF}_3]$, boratabenzene, and carborane unsubstituted or substituted with a halogen atom; and

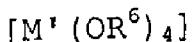
a and b are the number of the cations and anions,
25 respectively, and determined to allow the cation and anion to be electrically neutralized and balance the charges.

4. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 3, wherein the organic group containing the cation of Chemical Formula 4 is selected from the group consisting of ammoniums $[\text{NH}(\text{R}^5)_3]^+$, $[\text{NH}_2(\text{R}^5)_2]^+$, $[\text{NH}_3(\text{R}^5)_1]^+$, and $[\text{N}(\text{R}^5)_4]^+$ 5 phosphoniums $[\text{PH}(\text{R}^5)_3]^+$, $[\text{PH}_2(\text{R}^5)_2]^+$, $[\text{PH}_3(\text{R}^5)_1]^+$, and $[\text{P}(\text{R}^5)_4]^+$; carboniums $[\text{C}(\text{R}^5)_3]^+$; $[\text{H}(\text{OEt}_2)_2]^+$; $[\text{Ag}]^+$; and $[\text{Cp}_2\text{Fe}]^+$, in which R^5 is a linear or branched C_{1-20} alkyl group; an alkyl or silylalkyl group substituted with a halogen; a C_{3-12} cycloalkyl group unsubstituted or substituted with a hydrocarbon; a cycloalkyl or silyl cycloalkyl group substituted with a halogen; a C_{6-40} aryl group unsubstituted or substituted with a hydrocarbon; an aryl or silyl aryl group substituted with a halogen; a C_{7-15} aralkyl group unsubstituted or substituted with a hydrocarbon; or an aralkyl or silyl aralkyl group 15 substituted with a halogen.

5. The method for preparing a cycloolefin polymer
20 containing polar functional groups according to claim 3,
wherein the borate or aluminate of Chemical Formula 4 is an
anion represented by Chemical Formula 4a or 4b:

Chemical Formula 4a

25 [M' (R⁶)₄]

Chemical Formula 4b

wherein

5 M' is a boron or aluminum;
R⁶ is a halogen; a linear or branched C₁₋₂₀ alkyl or
alkenyl group unsubstituted or substituted with a halogen
atom; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted
with a halogen; a C₆₋₄₀ aryl group which unsubstituted or
10 substituted with a hydrocarbon; a C₆₋₄₀ aryl group
substituted with a linear or branched C₃₋₂₀ trialkylsiloxy
group or a linear or branched C₁₈₋₄₈ triarylsiloxy group; or
a C₇₋₁₅ aralkyl group unsubstituted or substituted with a
halogen.

15

6. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein the organic solvent is selected from the group
consisting of dichloromethane, dichloroethane, toluene,
20 chlorobenzene and mixtures thereof.

7. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein the total amount of the organic solvent is 50-400 %
25 by weight based on the total weight of the monomer
contained in the monomer solution.

8. The method for preparing a cycloolefin polymer

containing polar functional groups according to claim 1,
wherein the total amount of the organic solvent is 50-200 %
by weight based on the total weight of the monomer
contained in the monomer solution.

5

9. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein the polymerization reaction is performed at a
temperature of 80-170°C

10

10. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein the polymerization reaction is performed at a
temperature of 80-150°C

15

11. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein the catalyst mixture includes a metal catalyst
complex containing a cation complex made of the precatalyst
20 and the first cocatalyst and an anion complex made of the
second cocatalyst.

12. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
25 wherein the catalyst mixture comprises, based on 1 mole of
the precatalyst containing Group 10 transition metal, 1-3
moles of the first cocatalyst containing the organic

compound containing the Group 15 element; and 1-2 moles of the second cocatalyst which is capable of providing an anion and weakly coordinating to the metal of the precatalyst.

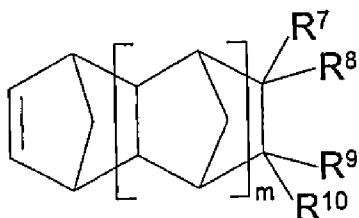
5

13. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the molar ratio of the catalyst mixture based on the Group 10 transition metal compound to the monomer 10 contained in the monomer solution is in the range of 1:2,500 - 1:100,000.

14. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, 15 wherein the polar functional group of the norborene-based compound includes an ester group and an acetyl group.

15. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, 20 wherein the norbornene-based compound containing a polar functional group is represented by the following Chemical Formula 5:

Chemical Formula 5

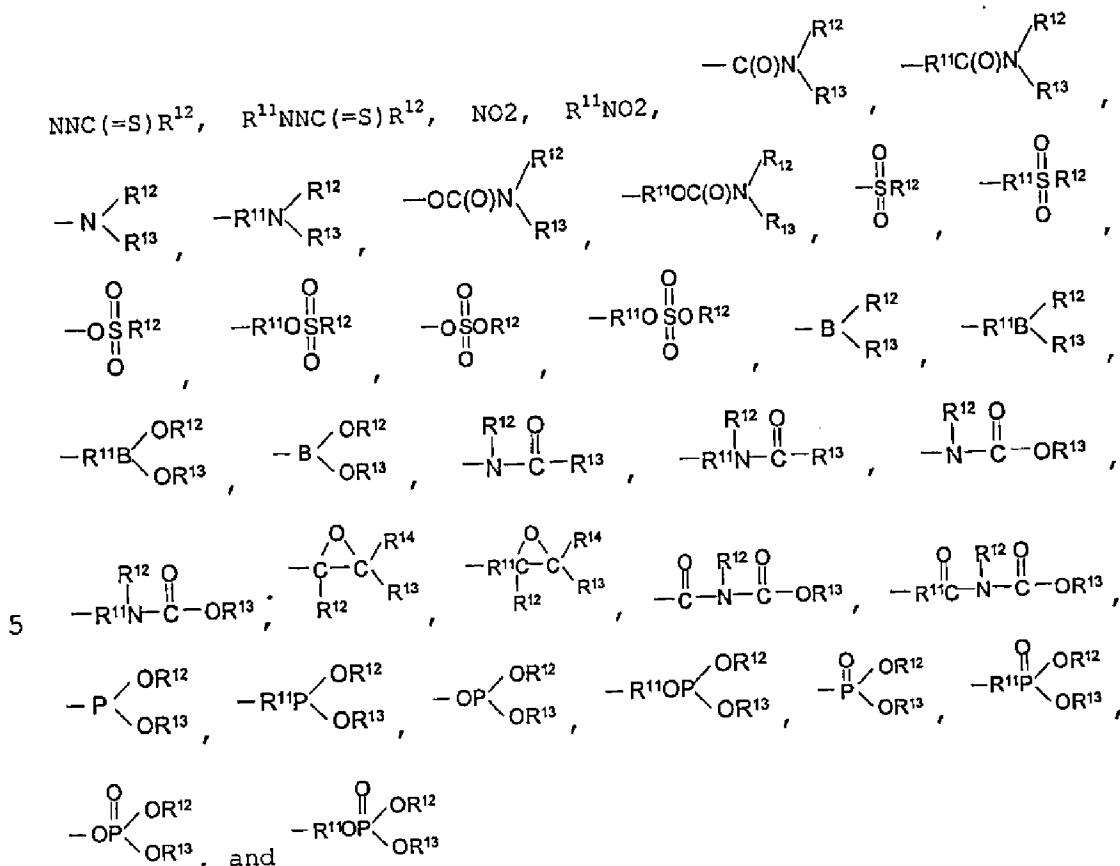


wherein

m is an integer of 0 to 4,
 at least one of R⁷, R⁸, R⁹ and R¹⁰ is a polar functional group, the others are non-polar functional group, and R⁷, R⁸, R⁹ and R¹⁰ can be bonded together to form a saturated or unsaturated C₁₋₂₀ cyclic group or C₆₋₂₄ aromatic ring;

the non-polar functional group includes hydrogen; halogen; a linear or branched C₁₋₂₀ alkyl group; , a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ or branched C₁₋₂₀ haloalkenyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; and a C₇₋₁₅ aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl;

the polar functional group is a non-hydrocarbonaceous polar group containing at least one of O, N, P, S, Si and B, and is selected from the group consisting of: OR^{12} , $OC(O)OR^{12}$, $R^{11}OC(O)OR^{12}$, $C(O)R^{12}$, $R^{11}C(O)R^{12}$, $OC(O)R^{12}$, $R^{11}OC(O)R^{12}$, $(R^{11}O)pOR^{12}$, $(OR^{11})pOR^{12}$, $C(O)OC(O)R^{12}$, $R^{11}C(O)OC(O)R^{12}$, SR^{12} , $R^{11}SR^{12}$, SSR^{12} , $R^{11}SSR^{12}$, $S(=O)R^{12}$, $R^{11}S(=O)R^{12}$, $R^{11}C(=S)R^{12}$, $R^{11}C(=S)SR^{12}$, $R^{11}SO_3R^{12}$, SO_3R^{12} , $R^{11}N=C=S$, NCO , $R^{11}NCO$, CN , $R^{11}CN$,



, in which R^{11} is a linear or branched C_{1-20} alkyl group;
 , a linear or branched C_{1-20} haloalkyl group; a linear or
 10 branched C_{1-20} alkenyl group; a linear or branched C_{1-20}
 haloalkenyl group; a linear or branched C_{3-20} alkynyl group;
 a linear or branched C_{3-20} haloalkynyl; a C_{3-12} cycloalkyl
 group unsubstituted or substituted with alkyl, alkenyl,
 alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a
 15 C_{6-40} aryl group unsubstituted or substituted with alkyl,
 alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or
 haloalkynyl; and a C_{7-15} aralkyl group unsubstituted or
 substituted with alkyl, alkenyl, alkynyl, halogen,
 haloalkyl, haloalkenyl, or haloalkynyl;
 20 R^{12} , R^{13} , and R^{14} are each independently hydrogen; a

halogen; a linear or branched C₁₋₂₀ alkyl group; , a linear or branched C₁₋₂₀ haloalkyl group; a linear or branched C₁₋₂₀ alkenyl group; a linear or branched C₁₋₂₀ haloalkenyl group; a linear or branched C₃₋₂₀ alkynyl group; a linear or branched C₃₋₂₀ haloalkynyl; a C₃₋₁₂ cycloalkyl group
5 unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a C₆₋₄₀ aryl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; a
10 C₇₋₁₅ aralkyl group unsubstituted or substituted with alkyl, alkenyl, alkynyl, halogen, haloalkyl, haloalkenyl, or haloalkynyl; or alkoxy, haloalkoxy, carbonyloxy, halocarbonyloxy; and

p is an integer of 1 to 10.

15

16. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 1, wherein the monomer solution further comprises a cycloolefin compound containing no polar functional group.

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17. The method for preparing a cycloolefin polymer containing polar functional groups according to claim 16, wherein the molar ratio of the cycloolefin compound containing no polar functional group is 30 % by mole based
25 on the total monomers contained in the monomer solution.

18. The method for preparing a cycloolefin polymer

containing polar functional groups according to claim 1,
wherein the cycloolefin polymer containing polar functional
groups includes a homopolymer of a cycloolefin monomer
containing a polar functional group, a copolymer of
5 cycloolefin monomers containing different polar functional
groups, and a copolymer of cycloolefin momomers containing
a polar functional group and cycloolefin monomers
containing no polar functional group.

10 19. The method for preparing a cycloolefin polymer
containing polar functional groups according to claim 1,
wherein a molecular weight (Mw) of the cycloolefin polymer
containing polar functional groups is in the range of
100,000-1,000,000.

15 20. An optical anisotropic film comprising a
cycloolefin polymer containing polar functional groups
which is prepared by a method as claimed in claim 1 and has
a molecular weight of 100,000 or more.

20 21. The optical anisotropic film according to claim
20, wherein the optical anisotropic film has 70 to 1000 nm
of a retardation value (Rth), as defined by the following
equation 1:

25 (Equation 1)

$$R_{th} = \Delta(n_y - n_z) \times d$$

wherein, n_y is a refractive index in a fast axis

direction in a plane, measured at a wavelength of 550 nm;
 n_z is a refractive index in a thickness direction,
measured at a wavelength of 550nm; and
 d is the film thickness.

5

22. The optical anisotropic film according to claim 20, the refractive index of the optical anisotropic film satisfies the following equation 3:

(Equation 3)

10 $nx \cong ny > nz$

wherein, nx is a refractive index in a slow axis direction in a plane, ny is a refractive index in a fast axis direction in the plane, and nz is a refractive index in a thickness direction.

15

23. The optical anisotropic film according to claim 22, wherein the optical anisotropic film is used as a negative C-plate type optical compensation film for Liquid Crystal Displays.

20

24. A display device comprising an optical anisotropic film as claimed in claim 20.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 03/02634-0

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08F 32/00, C08G 61/08, C09K 19/38, G02B 1/04, G02 F 1/333, G02B 5/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C08F, C08G, C09K, G02B, G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used):

EPODOC, WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6455650 B1 (LIPIAN et al.) 24 September 2002 (24.09.2002) (cited in the application). <i>claims 1,2,7,8,16&17; column 40, lines 19-59; column 43, line 56- column 44, line 6.</i>	1-24
X	WO 2002/088783 A1 (JSR CORPORATION) 7 November 2002 (07.11.2002) <i>claim 1; page 39, lines 7-15.</i>	20-24
X	WO 2002/088784 A2 (JSR CORPORATION) 7 November 2002 (07.11.2002) <i>claims 1,2,4,6; page 47, lines 10-18.</i>	20-24
X	US 5516456 A (SHINOHARA et al.) 14 May 1996 (14.05.1996) <i>claims 1 and 5.</i>	23

 Further documents are listed in the continuation of Box C. See patent family annex.

- * Special categories of cited documents:
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- „&“ document member of the same patent family

Date of the actual completion of the international search
10 February 2004 (10.02.2004)Date of mailing of the international search report
24 March 2004 (24.03.2004)Name and mailing address of the ISA/AT
Austrian Patent Office
Dresdner Straße 87, A-1200 Vienna
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PUSTERER F.
Telephone No. 1/53424/311

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 03/02634-0

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US A 5516456	1996-05-14	JP	A	7287123	1995-10-31
		JP	A	7287122	1995-10-31
US B 6455650	2002-09-24	ID	A	26727	2001-02-01
		US	A	2003181607	2003-09-25
		US	A	2003023013	2003-01-30
		US	A	2002052454	2002-05-02
		CN	T	1290275T	2001-04-04
WO A 20020887 83				none	
WO A 20020887 84				none	